

## BEAMLINE

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## PUBLICATION

S.E. Harton, T. Koga, F.A. Stevie, T. Araki, and H. Ade, "Investigation of Blend Miscibility of a Ternary PS/PCHMA/PMMA System using SIMS and Mean-Field Theory," *Macromolecules*, **38**, 10511-10515 (2005).

## FUNDING

National Science Foundation, U.S. Department of Energy

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## Miscibility in a Ternary Polymer System

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*The polymers poly(cyclohexyl methacrylate) (PCHMA) and polystyrene (PS) are miscible with each other, but each is highly immiscible with poly(methyl methacrylate) (PMMA). Due to their similar glass transition temperatures and the ability of PS and PCHMA to be controllably synthesized with a narrow molecular-weight distribution, we anticipate this blend to be a model system for future investigations of certain phenomena, such as diffusion in miscible blends and diffusion near surfaces and interfaces. As a first step, we have investigated the segregation of deuterated PS (dPS) from a miscible blend with PCHMA to a dPS:PCHMA/PMMA interface. We achieved this by recording real-space depth profiles of dPS with secondary ion mass spectrometry (SIMS). X-ray reflectometry was used to determine the interfacial roughness between PCHMA and PMMA.*

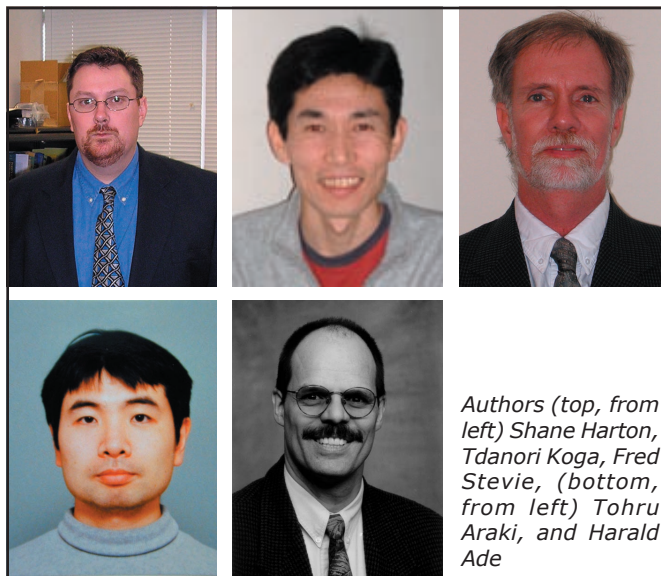
Miscible polymer blends have been model systems for investigations of polymer dynamics and equilibrium segregation at polymer surfaces and polymer/polymer interfaces. They are often composed of polymer pairs that have an apparent exothermic enthalpy of mixing. Previously investigated miscible blends have included polystyrene (PS) in combination with poly(xylenyl ether) (PXE), poly(vinylmethyl ether) (PVME), or tetramethylbisphenol-A polycarbonate (TMPC). These systems have constituents with highly different glass transition temperatures ( $T_g$ s). These asymmetries can lead to spatially varying  $T_g$ s, making accurate decoupling of various phenomena difficult. The need for a model miscible blend involving polymers with similar  $T_g$ s and well defined thermodynamic parameters has motivated this investigation.

To analyze the PCHMA/PMMA bilayers with x-ray specular reflectometry

(XR), single layers of PCHMA and PMMA were used at NSLS beamline X10B to individually measure the dispersion,  $\delta$ , of the two polymers. In the case of XR analysis of polymer bilayer systems, difficulties often arise in obtaining details regarding polymer-polymer interfaces due to the small x-ray contrast,  $\Delta\delta/\delta$ , between the individual polymers, which is typically less than 10% for most polymer pairs. In order to overcome this difficulty,

we used a Fourier transformation (FT) analysis method developed previously. A four-layer model (a silicon substrate, a native oxide layer, a PMMA layer, and a PCHMA layer) was used to fit the XR data. Using the measured values for  $\delta$ , the PCHMA/PMMA bilayers were analyzed using the FT method, as shown in **Figure 1**, and the interfacial roughness (Gaussian) was determined to be 0.6 nm. It should be noted that the x-ray contrast between PCHMA and PMMA is quite small (< 3%), and that this value is considered a lower limit.

In order to investigate segregation, deuterium depth profiles were acquired using a CAMECA IMS-6f magnetic sector secondary ion mass spectrometer (SIMS) with a 15 nA  $\text{Cs}^+$  primary beam (6.0 keV impact energy) rastered over a 200  $\mu\text{m}$  x 200  $\mu\text{m}$  area, with detection of negative secondary ions from a 60  $\mu\text{m}$  diameter circle at the center. The



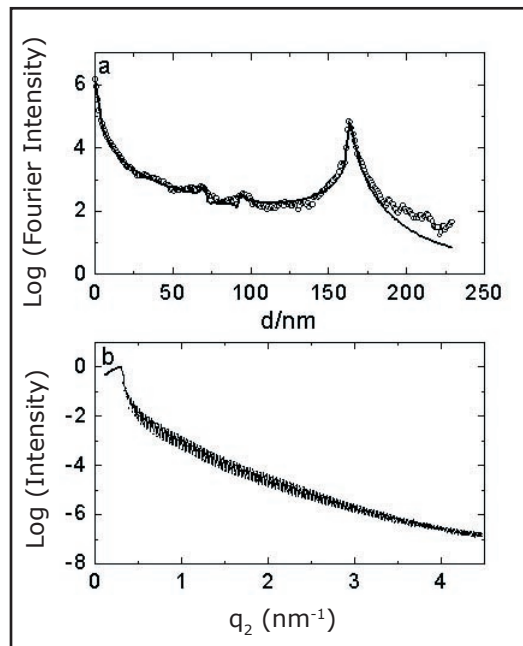
Authors (top, from left) Shane Harton, Tdanori Koga, Fred Stevie, (bottom, from left) Tohru Araki, and Harald Ade

analysis conditions used provided a nominal depth resolution (full width at half maximum) of 8 to 10 nm. From the phase behavior of the three polymer pairs, it is known that PS and PCHMA are completely miscible with each other, yet PS and PCHMA are completely immiscible with PMMA under the conditions implemented here. Taking advantage of these asymmetries in the thermodynamic interactions between dPS:PMMA and PCHMA:PMMA, dPS has been driven to the interface by annealing bilayer films at 150 °C for 42 hours. Using SIMS, the depth profiles were measured for initial dPS concentrations of 5,

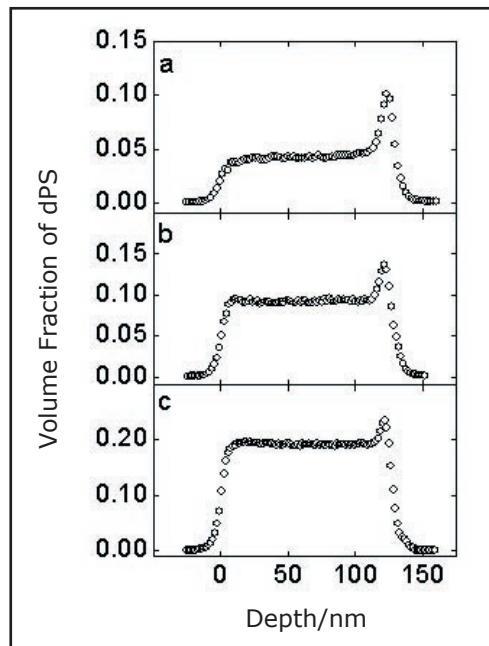
10, and 20% (v/v) in PCHMA, as shown in **Figure 2**. Because of the low interfacial excess (segregated dPS at the dPS:PCHMA/PMMA interface) observed, previously implemented techniques used to measure these depth profiles, such as forward recoil spectrometry or nuclear reaction analysis, would not be able to resolve the segregation of dPS to the dPS:PCHMA/PMMA interfaces, as their depth resolutions range from approximately 30 to 80 nm. Even with the relatively high depth resolution attainable using SIMS, it is difficult, if not impossible, to measure the interfacial roughness for highly

immiscible polymer bilayers. In contrast, XR can accomplish that, and SIMS and XR are excellent complementary tools.

Our work confirmed that PCHMA and PMMA are highly immiscible. Prior literature on the degree of miscibility of PS/PCHMA was inconsistent and large differences are reported for the interaction parameter that governs miscibility. Our segregation data agrees with the more highly miscible value, indicating that the PS/PCHMA system might be indeed an ideal model system for highly miscible polymers.



**Figure 1.** XR of PCHMA/PMMA bilayers. The Fourier method (a) was used to determine the interfacial roughness of this low contrast system. The low contrast is clearly observed in the reflectivity profile (b).



**Figure 2.** SIMS profiles for bilayers of dPS in PCHMA on PMMA with (a) 5, (b) 10, and (c) 20% (v/v) initial concentrations of dPS. After depletion of dPS due to segregation to the interface during the 42-hour anneal at 150° C, the bulk concentration away from the interface was reduced to (a) 4.3, (b) 9.2, and (c) 19.2%.